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Deep blue exciplex organic light emitting diodes with enhanced efficiency; *P*-type or *E*-type triplet conversion to singlet excitons?*By Vygintas Jankus,* Chien-Jung Chiang, Fernando Dias, and Andy Monkman*

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Abstract

In this paper we report simple trilayer deep blue fluorescent exciplex OLEDs where the majority of the emission is harvested from triplet excitons. Only two materials, N,N'-bis(1-naphthyl)N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and 1,3,5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi) as hole and electron transporting layers and a blend NPB and TPBi emission layer are used. These OLEDs emit from an exciplex state formed between the HOMO of NPB and LUMO of TPBi and NPB yielding 2.7% EQE at 450 nm. From steady state and time resolved PL and EL spectroscopy, and our previous findings on triplet dynamics and delayed fluorescence we show that the majority of the delayed emission in EL arises from *P*-type triplet fusion at NPB sites not *E*-type reverse intersystem crossing. We evaluate that the singlet production from triplet excitons has an efficiency of 33% showing how important singlet conversion from triplets via the triplet fusion channel can be in fluorescent blue OLEDs. We compare these results to recent reports of thermally assisted *E*-type delayed fluorescence in exciplex OLEDs.

Manuscript text

Since the discovery of organic light emitting diodes (OLEDs)¹ it has been assumed that the process of charge recombination to form excitons is controlled by random spin statistics and that singlet and triplet excitons are

formed in the ratio 1:3.²⁻⁴ This fundamentally limits external quantum efficiency of OLED devices, as 75% of excitons formed are triplet states which are weakly emissive.⁵ The external quantum efficiency of devices (EQE) depends on four factors:

$$EQE = \eta_{out} \cdot \eta_{fl} \cdot \gamma \cdot \eta_{fr} \quad (1.1)$$

where, η_{out} - light out coupling efficiency considered to be 20%.³⁻⁴ η_{fl} - fluorescence efficiency is usually assumed to be 1 as unity yield fluorescence emitters are possible,⁶ γ - charge balance factor can also be assumed to be 1 if highest occupied molecular orbital (HOMO) level, lowest unoccupied molecular orbital (LUMO) level of organic layers and workfunctions of electrodes are adjusted in an appropriate manner. η_{fr} - singlet formation ratio is assumed to be 25 % which limits the EQE to 5% ($EQE \sim 0.2 \cdot 1 \cdot 1 \cdot 0.25 = 0.05$). It is clear that one could increase the quantum efficiency of OLEDs fourfold by utilization of triplet excitons. This has been successfully achieved using heavy metal complexes as emissive dopants where phosphorescence efficiency is increased due to spin orbit coupling.⁷⁻⁸ There are many reports of near 100% internal QE (20-21% EQE) in phosphorescent OLEDs.⁷ However, it has been observed that blue emitting heavy metal complexes are unstable. For example, it was found that bis(4,6-difluorophenylpyridinato-N,C2)picolinatoiridium (FIrpic) degrades during vacuum deposition.⁹ Further, pushing the emissive MLCT band into the deep blue opens up additional non-radiative pathway via the metal d orbitals;¹⁰ this renders the synthesis of highly efficient deep blue phosphors very difficult. However, deep blue light is essential to achieve good colour rendering in white OLEDs for lighting applications,¹¹ hence other processes that can convert triplets to singlets must be investigated in order to achieve efficient deep blue OLEDs. For example, the production of singlets via triplet-triplet annihilation (TTA) *i.e.* triplet fusion (TF), has been successfully demonstrated in OLEDs.^{4, 12-14} E-type (thermally assisted) delayed fluorescence (E-DF) could also potentially be used in OLEDs. Here emitters with a small singlet-triplet gap (small electron exchange energy) enables triplets to undergo thermally activated reverse intersystem crossing back into the singlet manifold. This mechanism was reported in a copper complex emitter, yielding enhanced efficiency OLEDs.¹⁵ Recently, Goushi *et al*¹⁶ have used exciplex emitters, exploiting the fact the exciplexes have small exchange energies¹⁷, and demonstrated efficient triplet exciton harvesting via E-DF¹⁸

to increase OLED EQE substantially. In this paper, we report similar exciplex based OLEDs and show that the electroluminescence in our devices arises via exciplex emission enhanced with TF *not* E-DF, and explain why this is using time dependent photophysical studies of the exciplex emitter.

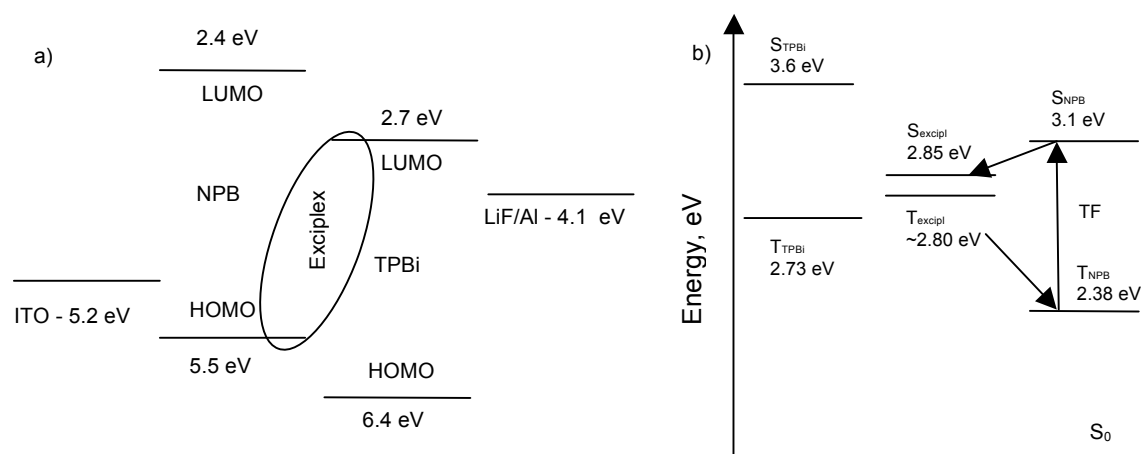


Figure 1. Energetics a) and singlet, triplet levels b) of main materials used, taken from references¹⁹⁻²². For singlet levels onset of fluorescence and for triplet the onset of phosphorescence spectra were taken. This is different for exciplex triplet which was taken to be at least 50 meV below singlet; the latter assignment rests on Goushi *et al* who found that the triplet of exciplex was ~ 50 meV below the singlet.¹⁶ Indeed it has been put forward by Weller³⁸ and Turro³⁹ that singlet-triplet splitting in exciplexes is negligible due to small electron exchange interaction. Proposed triplet recycling mechanism taking place after charge recombination to triplet state in an OLED is indicated using arrows.

Only two molecules were used in the blue OLEDs - N,N'-bis(1-naphthyl)N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and 1,3,5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi) (see Fig. 1). A blend NPB:TPBi layer was deposited between the NPB and TPBi charge transport layers which forms efficient exciplex states.^{16, 23} The singlet and triplet levels of NPB and TPBi and resulting exciplex are also depicted in Fig.1 with the exciplex having the lowest singlet level, whereas NPB has the lowest triplet level, here we assume that the exciplex state as an exchange energy of *ca.* 50-100 meV. The device structures tested were: glass/ITO/NPB (30nm)/NPB:TPBi (35nm)/TPBi (35nm)/LiF(1 nm)/Al(100 nm).

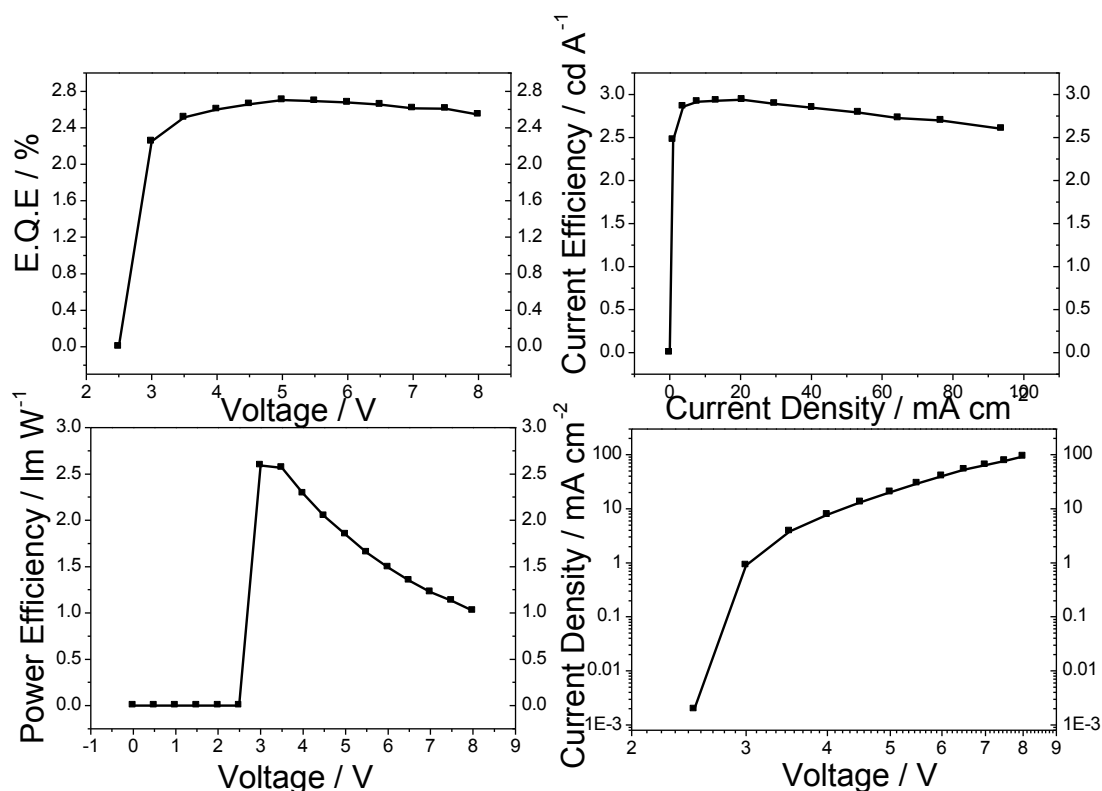


Figure 2. OLED device characteristics: EQE vs Voltage (top left), current efficiency vs current density (top right), power efficiency vs voltage (bottom left) and current density vs voltage (bottom right).

The J-V characteristic, current efficiency, power efficiency, EQE of the device are shown in Fig. 2. The device emits deep blue fluorescence with the CIE index of about (0.15, 0.13), λ_{EL} 450 nm, brightness of 600 cd/m², EQE of 2.7% and a very low turn-on voltage, 2.5 V. The low turn on voltage is indicative of direct charge injection into the exciplex HOMO-LUMO levels²⁴. The overall device efficiency is limited by the mismatch of ETL and HTL mobilities, with TPBi having an electron mobility some order of magnitude lower than the hole mobility of the NPB.²⁵ Another possible reason for this could be a high electron injection barrier, but the very low turn on voltage would not be consistent with this. The electroluminescence (EL) spectrum of the device is the same as photoluminescence (PL) spectrum recorded from NPB:TPBi (1:1) film (Fig. 3a) with the exception of a blue shoulder indicative of a small NPB emission contribution. The EL is redshifted to 450 nm (Fig. 2a) and much broader in comparison with pure NPB film PL spectra (peak at 439 nm). This is characteristic of

NPB:TPBi exciplex emission, $I_p-E_a=2.8$ eV (450 nm). Using an integrating sphere²⁶ we evaluated η_{fl} of NPB:TPBi (1:1) blend film to be 28 % and that of pure NPB film to be 35%. The later agrees well with literature values which are in the range of 30-40 %.²⁷⁻²⁸ Plugging these values into eq. (1) and assuming that only singlets are emissive i.e. $\eta_{\text{fr}}=25$ % yields a maximum possible EQE of 1.4 %. Hence we conclude that 50% of the EL must arise from singlets harvested from triplet states. This could happen either via TF or E-DF as depicted in Fig. 1b.

To determine which mechanism is responsible for the production of this ‘extra’ 50% of EL, we recorded PL transients and fluorescence decays from NPB and NPB:TPBi (1:1) films and EL transient from the OLED²⁹ (Fig. 3).

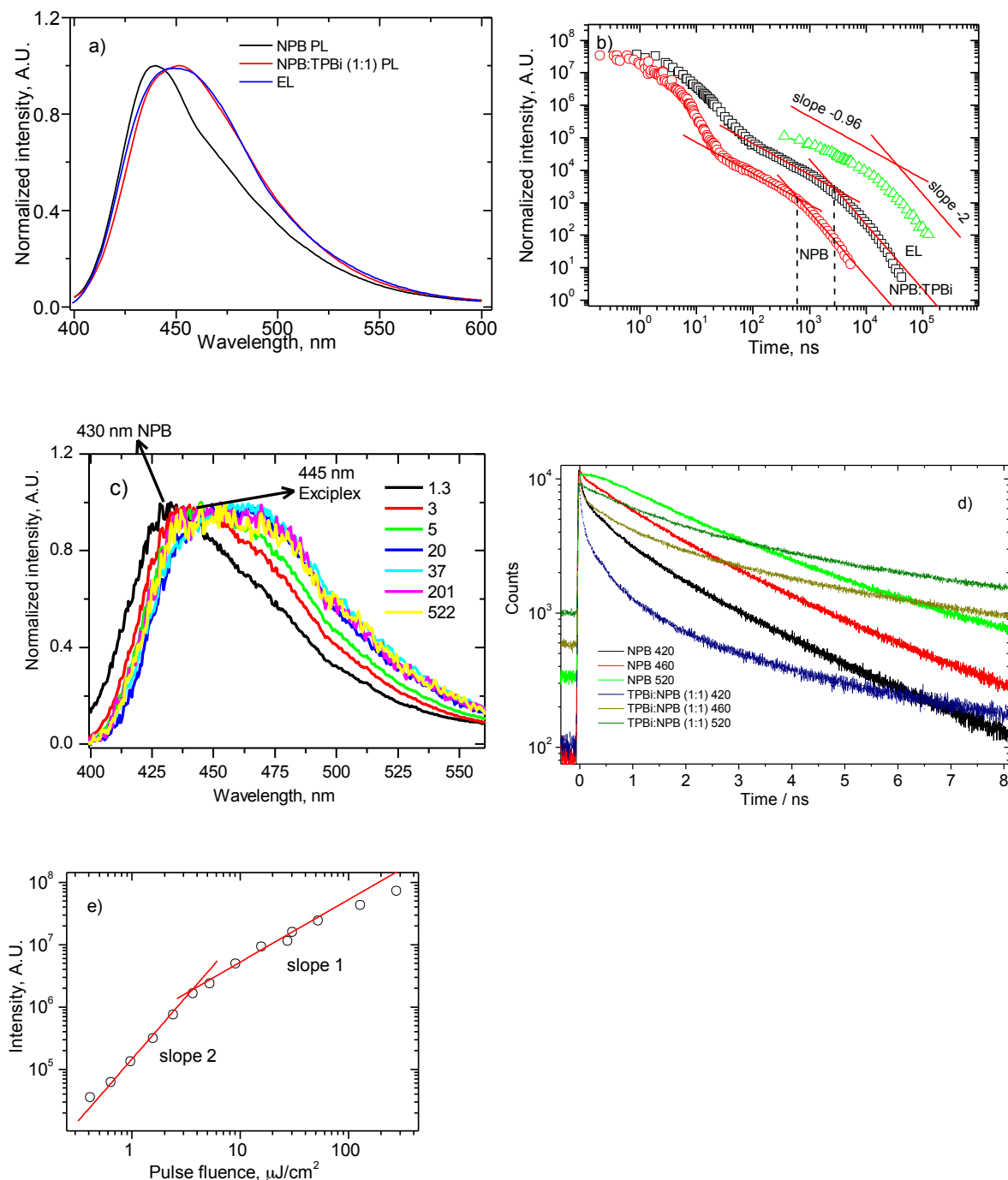


Figure 3. a) Photoluminescence spectra of NPB and NPB:TPBi (1:1) films, compared with the EL spectra from the device. The PL spectrum of TPBi:NPB 50:50 film is recorded exciting NPB only at 380 nm where TPBi does not absorb.³⁷ b) PL transients of pure NPB and NPB:TPBi (1:1) films excited at 355 nm, $60 \mu\text{J}/\text{cm}^2$ and EL transient of OLED excited with 9 V, 1 ms length pulse. Straight lines are power laws with slopes -0.96 and -2 and displayed as guides to an eye. Dashed lines denotes the transition times between dispersive and non-dispersive triplet migration regimes. c) Time resolved spectra from NPB:TPBi (1:1) film excited with 355 nm

pulsed laser and recorded with gated iCCD camera. Numbers indicate camera opening times after excitation in nanoseconds (delay time), the integration times are $\sim 1/10$ th of the delay time. d) Fluorescence decays of NPB and NPB:TPBi (1:1) films excited at 385 nm, $\sim 0.6 \text{ nJ/cm}^2$ recorded using single photon counting technique. e) Delayed PL emission intensity from NPB:TPBi (1:1) film dependence on laser pulse fluence at room temperature. Recorded from 400ns to 10 μs .

The DF and transient EL does not follow simple exponential dynamics (Fig. 3b), but rather a more complicated decay with two power law exponents, initially decaying with a slope *ca.* -1, which at later times turns over to a slope -2. These are characteristic to DF decays arising from TF. The slope -2 can be explained using the classical diffusion equation describing triplet dynamics, as we have previously shown, see supporting information.^{20, 30}

Hence if TF is responsible for the DF and long lived EL transient, they should both follow a power law intensity dependence having an exponent -2 (if triplet migration is non-dispersive i.e. k_{tt} is time-independent^{20, 30}). This is observed at later times in EL transient and in PL of both NPB:TPBi 1:1 and pure NPB films (Fig. 3b). In the initial time region, however, the decay follows slope *ca.* -1. Such decay dynamics are commonly observed in other organic films, *e.g.* polyfluorene³⁰ and NPB itself²⁰ and have been ascribed to the effect of dispersive migration of the triplet population. This happens when triplets generated randomly in the density of states (DOS) relax towards the tail of the DOS, making k_{tt} time-dependent. We also note that transition between dispersive and non-dispersive regimes (time at which slope *ca.* -1 turns into slope -2) in the PL transient of NPB:TPBi 1:1 blend is observed to occur later than in the PL transient of NPB film. This is due to larger energetic disorder in blended NPB:TPBi film that should be more amorphous than single component NPB film; for more disordered materials turnover between non-dispersive and dispersive regime is expected to be observed at later times.⁴⁰ A slight deviation from slope -2 in PL transient from NPB:TPBi film is observed at very late times. Similar deviations has been recorded in polyfluorene previously and has been explained by greater importance of monomolecular decay pathways at such late times.

Further, we have recorded PL DF intensity dependence at low excitation and high excitation fluencies (Fig 3e). DF arising from TF must follow a quadratic dependence on the initial triplet concentration (or laser pulse

intensity) exactly as observed. At higher excitation densities this turns over to a linear relationship as then TF is dominant within a large population of triplet states; this is in line with previous observations of DF arising via TF in other organic films, including NPB.^{20, 30}

Fluorescence decay curves are given in Fig. 3d and fitted lifetimes (at 460 nm) can be found in Supporting Information table S1. Pure NPB film decays with very similar rates across the emission band, at 420 nm, 460 nm and 520 nm, with some minor differences at initial times, which can be ascribed to singlet energy migration in the density of states.³¹ However, fluorescence from NPB:TPBi (1:1) films decays in a very different manner. At the blue edge (420 nm) initially it decays rapidly (<0.1 ns) and at later times this turns to a single long exponential decay in the order of nanoseconds. This long decay is characteristic of exciplex decay which normally are longer lived than the parent molecules.¹⁶ At 520 nm the longer component is more substantial in the overall decay pattern with a very small contribution from the fast component confirming that more emission is coming from the red shifted exciplex. Hence, we conclude that in NPB:TPBi (1:1) film we record a mix of NPB molecular fluorescence decay (fast component 23 ps at $\lambda_{em}=460$ nm) and exciplex fluorescence decay (slow component 3.5 ns at $\lambda_{em}=460$ nm). The fast NPB decay component in a blend film is much faster than NPB decay in a pure film (2.2 ns at $\lambda_{em}=460$ nm) indicating quenching of NPB singlet state by electron transfer to form the exciplex, which has the lowest singlet state in a system. Exciplex formation in the solid state is thus relatively a slow process which we can resolve here.

Room temperature time resolved emission of NPB film shows a very small contribution from an excimer (*ca.* 475 nm)³² in the μ s time regime (see supporting information S1 and S2) but primarily PF and DF from TF yielding 'singlet' emission up to 1000 ns and longer, NPB clearly gives efficient TF³³. Time resolved spectra from 1:1 NPB:TPBi blend shows initial NPB emission (430 nm) which rapidly turns over to exciplex emission (~445 nm) within the first few nanoseconds (Fig. 3c). Exciplex emission is observed for the next microsecond. At long times (>2 μ s, see supplementary data S3), a very weak new emission is detected, centred at *ca.* 475-500 nm. The 475 nm peak in fig 3 c has different decay kinetics than that seen at 445 nm and is also seen in pure NPB (supplementary data S3). This leads us to believe this is NPB excimer not exciplex triplet - Weller³⁸ proposed that CT singlet and triplet will be nearly isoenergetic and so unresolvable in these long time spectral decays. At 15 K the blend again gives very strong exciplex emission preceded by NPB singlet emission. At later

times (millisecond) clear NPB phosphorescence is observed alongside the exciplex emission, what indicates that the NPB triplet state is quenching the exciplex triplet (see supporting information S3). No shift of the exciplex emission is observed.

Thus, given the energy and HOMO LUMO diagrams (Fig. 1), the efficient TF measured in NPB, and the early time PL data where NPB fluorescence is observed before exciplex formation quenches singlet NPB states, we can fully understand the EL spectra of the NPB:TPBi devices. Singlet states formed on recombination (potentially direct exciplex states given the very low turn on voltage but also NPB excitons) will either emit or ISC to a triplet state, in the case of near iso energetic singlet and triplet exciplex states this will be efficient (giving a low singlet exciplex PLQY). The vast majority of exciplex triplet states formed by charge recombination will be quenched by the lower lying NPB triplet state. Thus most excited states formed on charge recombination will rapidly end up as NPB triplet excitons. These NPB triplets then undergo efficient TF (singlet generation efficiency 0.2^{12-13}) generating NPB singlets in the blend, some of which decay before forming exciplex singlet states again, and so on round this loop. Thus we can interpret the complex device EL spectra and account for the high efficiency through the large contribution of TF in this case. Using equation (1) we can estimate the contribution to the total EL of each of these steps;

Direct singlet contribution; $0.25 \times 0.2 \times 0.28 = 0.014$

TF contribution; $0.75 \times 0.2 \times 0.2 \times 0.28 = 0.0084$

ISC component; $0.25 \times (1 - 0.28) \times 0.2 \times 0.2 \times 0.28 = 0.002$

Giving a total estimate for the device EQE of 0.025, very close to the value of 0.027 we measure which is far greater than that which we would expect simply from only the direct singlets (form on recombination). Adding in another contribution due to those delayed singlets that ISC will increase our estimate even closer to the device result. We note, that in figure 2, the EL efficiency increases with voltage or current and then rolls of a little. This can be explained by the fact that exciton annihilation can contribute to both increase (TF) and loss (singlet triplet annihilation, STA) in an OLED and this just has been shown in very recent publication by Zhang *et al.*³⁴

In conclusion, we have fabricated very simple structured, two material trilayer deep blue OLEDs which give efficiencies (2.7% EQE) at 450 nm, twice as high as 25% singlet production predicts (1.4% EQE). We show that the majority of the EL is harvested from triplet excitons via triplet fusion. From the EL characteristics and PL spectra we deduce that the charges recombine in the blend layer via direct injection into the exciplex state as well as potentially forming NPB excitons, yielding blue emission at low turn on voltage, 2.5 V. From PL and EL transient measurements and previous triplet dynamics and delayed fluorescence work on NPB photophysics²⁰ we show that the majority of the delayed fluorescence in both PL and EL arises from triplet fusion on NPB sites, which then reform exciplex states, the DF yields both NPB fluorescence and exciplex emission. Our results show the importance of triplet fusion in producing efficient deep blue fluorescence OLEDs and that with improved photoluminescence quantum yield of the exciplex state it could lead to 12 % EQE blue exciplex OLEDs. Further, this form of triplet harvesting also makes use of those singlet states which cross to triplets as well. We note here though that in the case of the NPB:TPBi exciplex, the NPB triplet state is lower in energy than the exciplex triplet and so is rapidly quenched by the latter. This may be different to the recent reports by Goushi and Adachi³⁵ given that in their exciplex devices such triplet quenching may not be efficient.

Experimental

OLED devices were fabricated using pre-cleaned indium-tin-oxide (ITO) coated glass substrates purchased from Visiontek with a sheet resistance of $15 \Omega/\text{cm}^2$ and ITO thickness of 150 nm. They were patterned so that the OLED devices had a pixel size of 10 mm by 10 mm. The small molecule and cathode layers were thermally evaporated using the Kurt J. Lesker Spectros II deposition at 5×10^{-7} mbar. All materials were deposited at a rate of 1 \AA s^{-1}

PL transients were recorded exciting films at 355 nm with 150 ps length YAG laser (EKSPLA) pulses and collecting light using Jobin Yvon spectrograph and gated ICCD camera (Stanford Computer Optics) by exponentially increasing delayed and integration times as described in ref³⁰. This allows to record up to 10 orders of magnitude in time and intensity of the PL decay.²⁰ For EL transient same light collection setup and data collection method was employed and as excitation source HP 8114A pulse generator was used (9 V, length 1 ms). Time-resolved fluorescence decays were collected using the picosecond time-correlated single photon

counting technique (impulse response function, IRF=21 ps). The excitation source, was a picosecond Ti:Sapphire laser from Coherent Inc., (wavelength range: 720 to 1000 nm, 76 MHz repetition rate) coupled to a second harmonic generator (360 to 500 nm). Emission was detected by a Hamamatsu microchannel plate (MCPT) model R3809U-50 through a double subtractive monochromator SpectraPro-2300i (Acton Research Corporation). Signal acquisition was performed using a TCSPC module from Becker & Hickl (Model SPC-630) using 4096 channels in a 0.8 ps per channel timescale ³⁶. All data was recorded at room temperature unless stated otherwise.

Acknowledgements

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References

- [1] C. W. Tang, S. A. Vanslyke, *Appl. Phys. Lett.* 1987, 51, 913.
- [2] P. W. Atkins, *Molecular Quantum Mechanics*, Oxford University Press, 1983.
- [3] Z. Kafafi, Ed. *Organic Electroluminescence*, Taylor & Francis Group, LLC, 2005.
- [4] D. Y. Kondakov, *J. Appl. Phys.* 2007, 102, 114504
- [5] J. B. Birks, *The Photophysics of Aromatic Molecules*, John Wiley & Sons Ltd, London 1970.
- [6] T. Aimono, Y. Kawamura, K. Goushi, H. Yamamoto, H. Sasabe, C. Adachi, *Appl. Phys. Lett.* 2005, 86, 071110.
- [7] C. Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, *J. Appl. Phys.* 2001, 90, 5048.
- [8] C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* 2001, 79, 2082.
- [9] V. Sivasubramaniam, F. Brodkorb, S. Hanning, H. P. Loebl, V. van Elsbergen, H. Boerner, U. Scherf, M. Kreyenschmidt, *J. Fluor. Chem.* 2009, 130, 640.
- [10] L. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwert Academic / Plenum Pyblishers, New York 1999.
- [11] K. T. Kamtekar, A. P. Monkman, M. R. Bryce, *Adv. Mater.* 2010, 22, 572.
- [12] D. Y. Kondakov, *J. Soc. Inf. Disp.* 2009, 17, 137.
- [13] D. Y. Kondakov, T. D. Pawlik, T. K. Hatwar, J. P. Spindler, *J. Appl. Phys.* 2009, 106, 124510
- [14] S. M. King, M. Cass, M. Pintani, C. Coward, F. B. Dias, A. P. Monkman, M. Roberts, *J. Appl. Phys.* 2011, 109, 074502.
- [15] J. C. Deaton, S. C. Switalski, D. Y. Kondakov, R. H. Young, T. D. Pawlik, D. J. Giesen, S. B. Harkins, A. J. M. Miller, S. F. Mickenberg, J. C. Peters, *J. Am. Chem. Soc.* 2010, 132, 9499.
- [16] K. Goushi, K. Yoshida, K. Sato, C. Adachi, *Nat Photon* 2012, 6, 253.
- [17] Wellar A., *The Exciplex*, Academic Press Inc., New York 1975.
- [18] B. Frederichs, H. Staerk, *Chem. Phys. Lett.* 2008, 460, 116.
- [19] R. Pode, S.-J. Lee, S.-H. Jin, S. Kim, J. H. Kwon, *J. Phys. D-Appl. Phys.* 2010, 43.
- [20] V. Jankus, C. Winscom, A. P. Monkman, *J. Phys.-Condes. Matter* 2010, 22, 185802.
- [21] S.-y. Takizawa, V. A. Montes, P. Anzenbacher, *Chemistry of Materials* 2009, 21, 2452.
- [22] Y. Liu, M. Nishiura, Y. Wang, Z. Hou, *J. Am. Chem. Soc.* 2006, 128, 5592.
- [23] W. M. Su, W. L. Li, Q. Xin, Z. S. Su, B. Chu, D. F. Bi, H. He, J. H. Niu, *Applied Physics Letters* 2007, 91, 3.
- [24] A. C. Morteani, A. S. Dhoot, J. S. Kim, C. Silva, N. C. Greenham, C. Murphy, E. Moons, S. Cina, J. H. Burroughes, R. H. Friend, *Adv. Mater.* 2003, 15, 1708.
- [25] I. W. Wu, P.-S. Wang, W.-H. Tseng, J.-H. Chang, C.-I. Wu, *Org. Electron.* 2012, 13, 13.
- [26] L. O. Palsson, A. P. Monkman, *Adv. Mater.* 2002, 14, 757.
- [27] Y. Kawamura, H. Yamamoto, K. Goushi, H. Sasabe, C. Adachi, H. Yoshizaki, *Appl. Phys. Lett.* 2004, 84, 2724.
- [28] H. Mattoussi, H. Murata, C. D. Merritt, Y. Iizumi, J. Kido, Z. H. Kafafi, *J. Appl. Phys.* 1999, 86, 2642.
- [29] S. Sinha, C. Rothe, R. Guntner, U. Scherf, A. P. Monkman, *Phys. Rev. Lett.* 2003, 90, 127402.
- [30] C. Rothe, A. P. Monkman, *Phys. Rev. B* 2003, 68, 075208.
- [31] S. C. J. Meskers, J. Hubner, M. Oestreich, H. Bassler, *Chem. Phys. Lett.* 2001, 339, 223.
- [32] P. A. Losio, R. U. A. Khan, P. Gunter, B. K. Yap, J. S. Wilson, D. D. C. Bradley, *Appl. Phys. Lett.* 2006, 89, 041914.
- [33] V. Jankus, C. Winscom, A. P. Monkman, *Adv. Funct. Mater.* 2011, 21, 2522.
- [34] Y. Zhang, S. R. Forrest, *Phys. Rev. Lett.* 2012, 108, 267404.
- [35] Goushi K., Adachi C., *Appl. Phys. Lett.* 2012, in press.
- [36] A. Monkman, C. Rothe, S. King, F. Dias, in *Polyfluorenes*, Vol. 212, 2008, 187.
- [37] G. Zhang, W. Li, B. Chu, Z. Su, D. Yang, F. Yan, Y. Chen, D. Zhang, L. Han, J. Wang, H. Liu, G. Che, Z. Zhang, Z. Hu, *Org. Electron.* 2009, 10, 352.
- [38] M. Gordon, W.R. Ware, Eds., *The Exciplex*, Academic Press Inc., New York, San Francisco, London 1975, page 32.

- [39] N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Company, Inc, Menlo Park, California 1978.
- [40] B. Ries, H. Bassler, M. Grunewald, B. Movaghar, Phys. Rev. B 1988, 37, 5508.

Figures

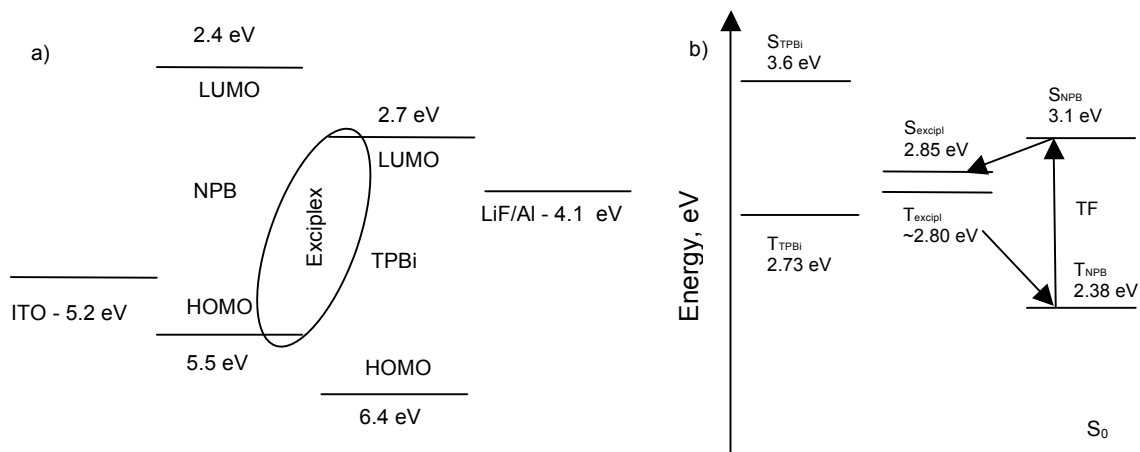


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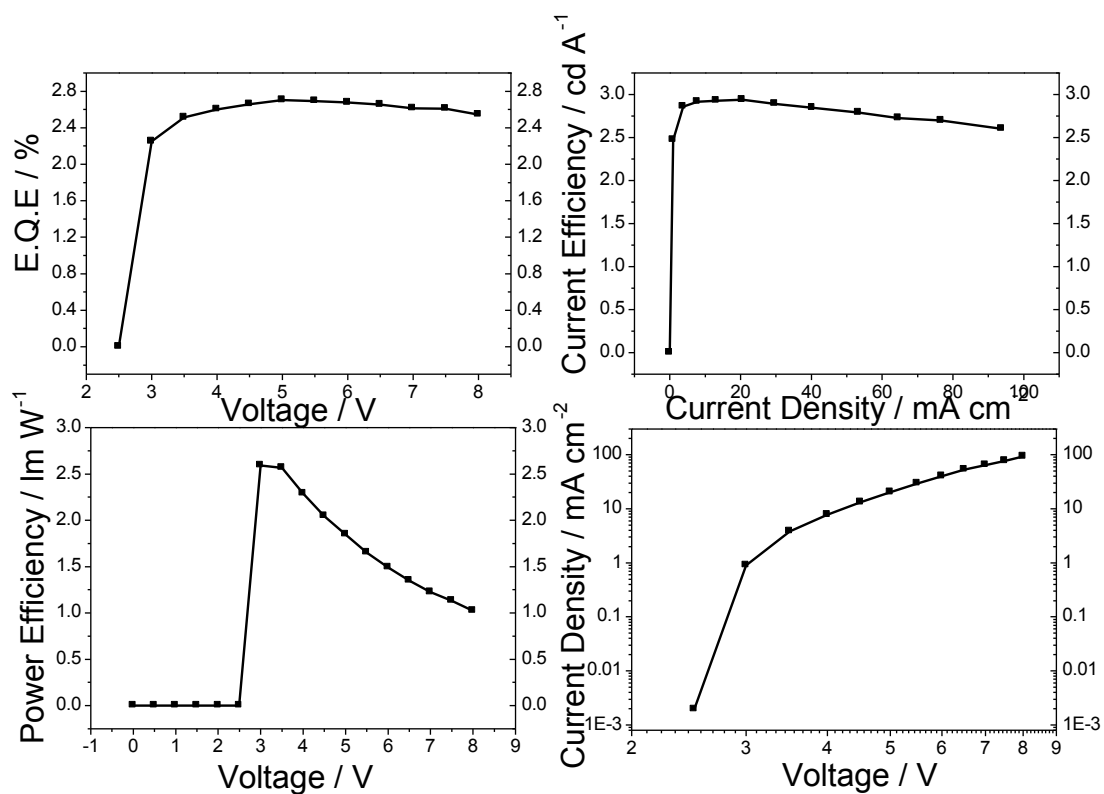


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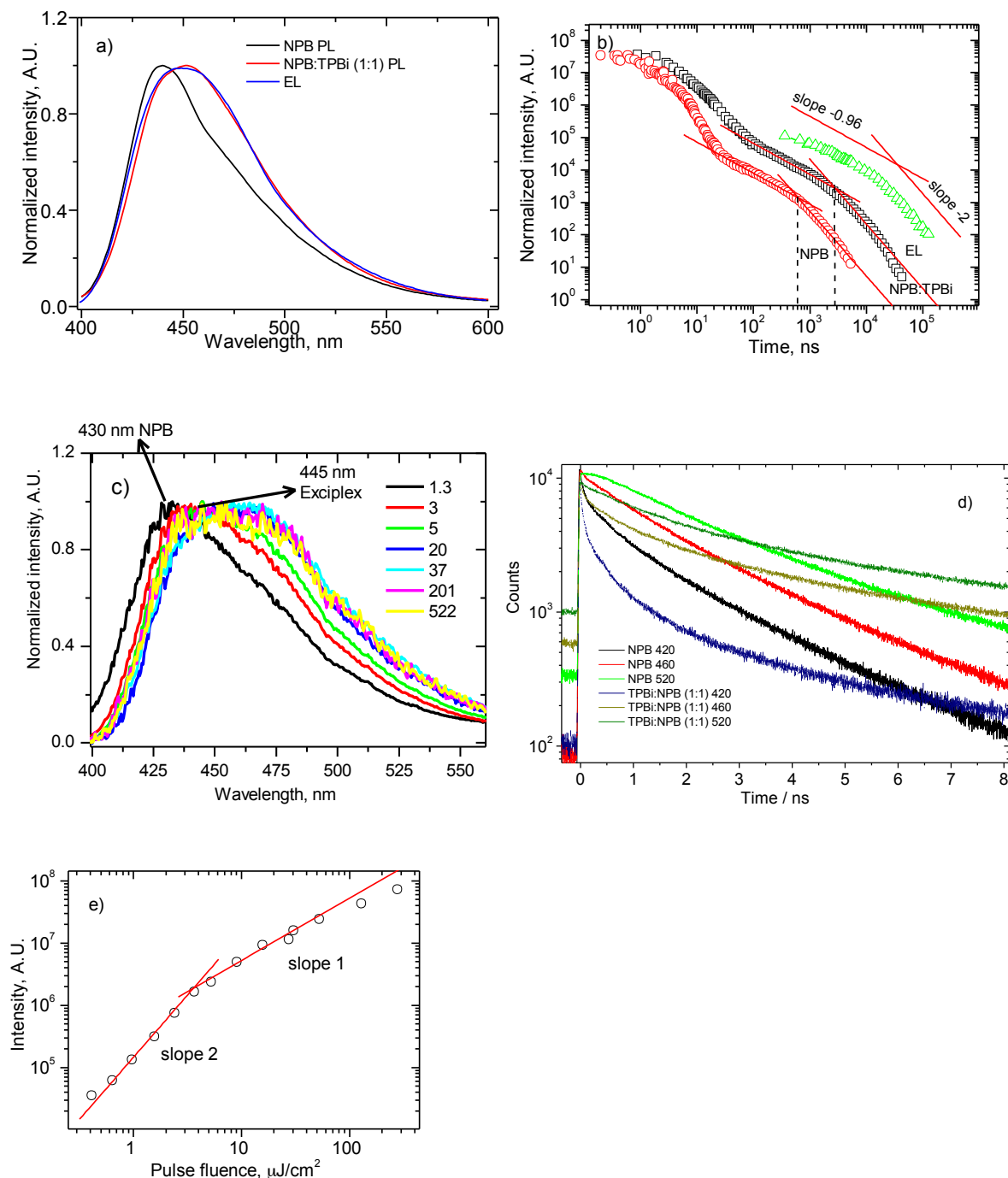


Figure 3. a) Photoluminescence spectra of NPB and NPB:TPBi (1:1) films, compared with the EL spectra from the device. The PL spectrum of TPBi:NPB 50:50 film is recorded exciting NPB only at 380 nm where TPBi does not absorb.³⁷ b) PL transients of pure NPB and NPB:TPBi (1:1) films excited at 355 nm, $60 \mu\text{J}/\text{cm}^2$ and EL transient of OLED excited with 9 V, 1 ms length pulse. Straight lines are power laws with slopes -0.96 and -2 and displayed as guides to an eye. Dashed lines denotes the transition times between dispersive and non-dispersive triplet migration regimes. c) Time resolved spectra from NPB:TPBi (1:1) film excited with 355 nm

pulsed laser and recorded with gated iCCD camera. Numbers indicate camera opening times after excitation in nanoseconds (delay time), the integration times are $\sim 1/10$ th of the delay time. d) Fluorescence decays of NPB and NPB:TPBi (1:1) films excited at 385 nm, $\sim 0.6 \text{ nJ/cm}^2$ recorded using single photon counting technique. e) Delayed PL emission intensity from NPB:TPBi (1:1) film dependence on laser pulse fluence at room temperature. Recorded from 400ns .. 10 μs .

Supporting Information**Deep blue exciplex organic light emitting diodes with enhanced efficiency; *P-type* or *E-type* triplet conversion to singlet excitons?**

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1. Power law with the slope -2 explanation.

The majority of the EL transient emission comes from very long lived component (Fig. 3b). The EL transient follows not simple exponential dynamics, but rather a more complicated decay with two power law exponents, initially decaying with a slope ~ -1 , which later turns to a slope -2 , that are characteristic to DF decays arising from TF. The slope -2 can be explained by using the classical diffusion equation describing the triplet dynamics. First, we assume that triplet concentration at time 0 is $[T] = [T_0]$. This is then depopulated by monomolecular processes i.e. radiative decay at a rate k_r and non radiative decay rate k_{nr} as well as by bimolecular processes, such as TTA at a rate k_{tt} :¹⁻³

$$\frac{d[T]}{dt} = -(k_{nr} + k_r)[T] - k_{tt}[T]^2 \quad (S1)$$

If we consider that the excitation intensity is high leading to triplet dynamics dominated by TTA, then monomolecular processes can be neglected. One can then solve for $[T]$, considering k_{tt} being time-independent, to get

$$[T] = \frac{[T_0]}{(1 + k_{tt}[T_0]t)} \sim t^{-1} \quad (S2)$$

Further, from equation (S2) we can derive the delayed fluorescence dependence on time. If TF is the dominant process in the system then the delayed fluorescence (DF) intensity should be proportional to the square of the triplet population over time:

$$DF \sim k_{tt}[T]^2 = k_{tt}[T_0]^2 \frac{1}{(1 + k_{tt}[T_0]t)^2} \quad (S3)$$

At high intensities and moderately long times $k_{tt}[T_0]t \gg 1$ leading to

$$DF \sim \frac{k_{tt}[T_0]^2}{(k_{tt}[T_0]t)^2} \sim t^{-2} \quad (S4)$$

However sometimes k_{tt} is time dependent that happens when triplets generated randomly in the density of states (DOS) relax towards the tail of the DOS and then triplet migration is called to be dispersive. In such circumstances eq. (S1) and its solutions cannot be used to describe the process and more complicated theories need to be employed.⁴⁻⁷ It has been shown numerous times that the process of a triplet population migrating in a dispersive manner cannot be cast into a simple analytical expression and this -1 slope assignment to dispersive triplet migration is drawn from the entirety of evidence, namely, experimental results,¹⁻³ Monte-Carlo simulations⁸⁻⁹ and theoretical solutions derived using limiting assumptions.⁵

2. Time resolved spectra of PL and EL emission.

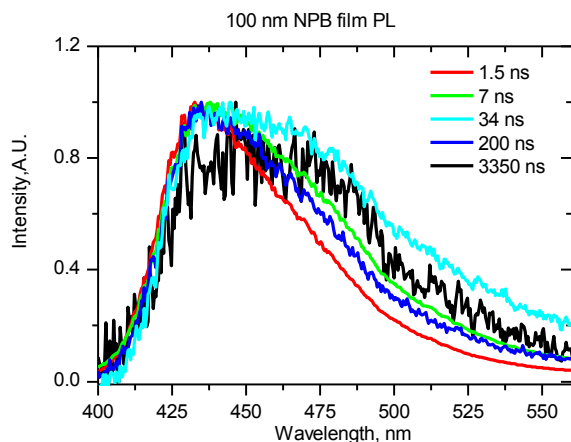


Figure S1. Time resolved spectra from 100 nm NPB film excited with 355 nm pulsed laser and recorded with a gated iCCD camera at room temperature. Numbers indicate camera opening times after excitation (delay time), whereas the integration times are $\sim 1/10$ th of the delay time.

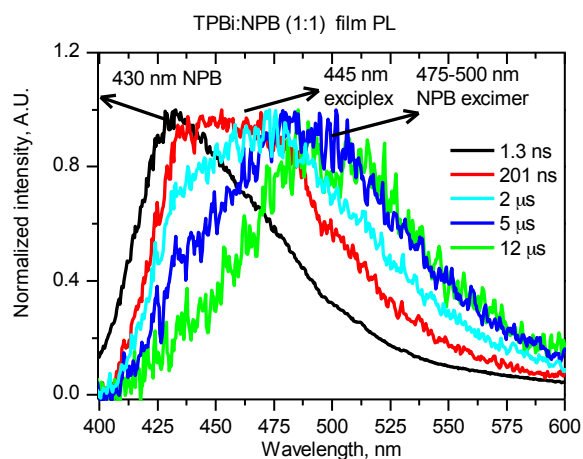


Figure S2. Time resolved spectra from TPBi:NPB (1:1) film excited with 355 nm pulsed laser and recorded with a gated iCCD camera at room temperature. Numbers indicate camera opening times after excitation (delay time), whereas the integration times are $\sim 1/10$ th of the delay time. At 430 nm NPB emission is observed, at 445 nm TPBi NPB exciplex emission and at 500 nm exciplex phosphorescence (PH) or NPB excimer¹⁰.

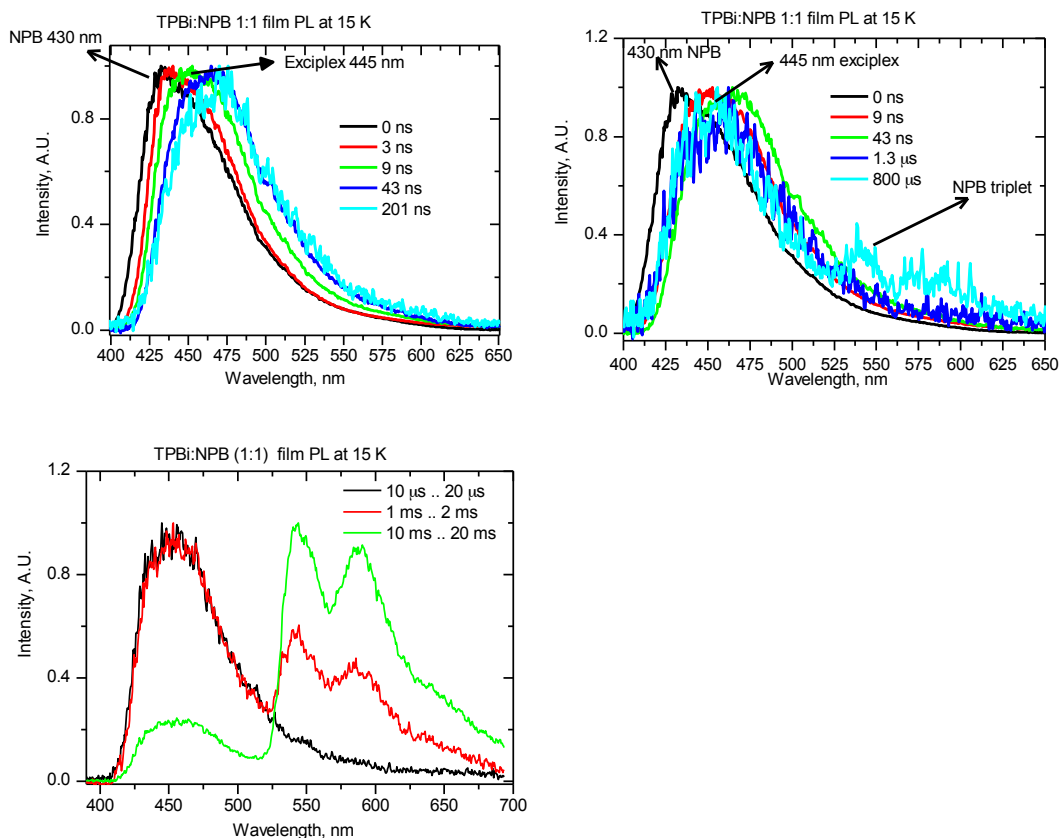


Figure S3. Time resolved spectra from TPBi:NPB (1:1) film excited with 355 nm pulsed laser and recorded with a gated iCCD camera at 15 K. At the top numbers indicate camera opening times after excitation (delay time), whereas the integration times are $\sim 1/10$ th of the delay time. At the bottom numbers indicate camera opening and closing times after excitation. At 430 nm NPB singlet emission is observed, at 445 nm TPBi NPB exciplex emission and at 540 nm NPB triplet emission³.

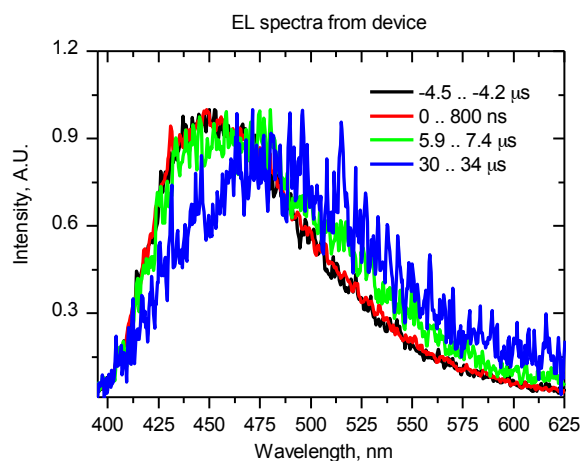


Figure S4. Time resolved spectra from OLED device excited with 9V 1 ms length pulse and recorded with gated iCCD camera. The numbers indicate camera opening and closing times after excitation. Zero time is considered as the time when EL starts to decay.

3. Fluorescence decay lifetimes

Table S1. Fluorescence decay lifetimes recorded using single photon counting technique exciting at 385 nm (in nanoseconds).

Film	$\tau_1[A_1]$	$\tau_2[A_2]$	$\tau_3[A_3]$	$\tau_4[A_4]$
100 nm pure NPB $\lambda_{em}=460$ nm	0.174 (0.17)	0.822 (0.25)	2.207 (0.58)	----
100 nm pure NPB:TPBi (1:1) $\lambda_{em}=460$ nm	0.023 (0.2)	0.174 (0.24)	0.822(0.23)	3.537 (0.33)

References

- [1] D. Hertel, H. Bassler, R. Guentner, U. Scherf, J. Chem. Phys. 2001, 115, 10007.
- [2] C. Rothe, A. P. Monkman, Phys. Rev. B 2003, 68, 075208.
- [3] V. Jankus, C. Winscom, A. P. Monkman, J. Phys.-Condes. Matter 2010, 22, 185802.
- [4] B. Movaghar, M. Grunewald, B. Ries, H. Bassler, D. Wurtz, Phys. Rev. B 1986, 33, 5545.
- [5] B. Movaghar, B. Ries, M. Grunewald, Phys. Rev. B 1986, 34, 5574.
- [6] M. Grunewald, B. Pohlmann, B. Movaghar, D. Wurtz, Philos. Mag. B-Phys. Condens. Matter Stat. Mech. Electron. Opt. Magn. Prop. 1984, 49, 341.
- [7] R. Richert, H. Bassler, B. Ries, B. Movaghar, M. Grunewald, Philos. Mag. Lett. 1989, 59, 95.
- [8] B. Ries, H. Bassler, M. Grunewald, B. Movaghar, Phys. Rev. B 1988, 37, 5508.
- [9] M. Scheidler, B. Cleve, H. Bassler, P. Thomas, Chem. Phys. Lett. 1994, 225, 431.
- [10] P. A. Losio, R. U. A. Khan, P. Gunter, B. K. Yap, J. S. Wilson, D. D. C. Bradley, Appl. Phys. Lett. 2006, 89.